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INCREASING THE STRENGTH OF REFRACTORY GRANULES BY APPLYING PROTECTIVE SILICATE COATING

E. L. Murav'eva¹ and G. D. Yankin¹Translated from *Steklo i Keramika*, No. 10, pp. 37–38, October, 2002.

The fundamental possibility of increasing the strength of refractory granules by 1.5–2 times by applying coatings based on organosilicon compounds at elevated temperatures is demonstrated. It is established that the increase in strength is to a large extent achieved by producing coating with a finely crystalline structure of sodium silicate, silicon oxide, or glass; the strength of granules increases as the coating thickness increases; at the same time, the hydrophoby of granules becomes higher.

The propants used lately as propping liquids for oil wells constitute a granulated sintered product based on alumina-bearing material with fillers. Propping agents, like all refractories, have a certain (as a rule, 15–25%) porosity, which decreases their strength under the effect of moisture and compressive loads. Consequently, it is very important to find ways to increasing the strength and hydrophoby of propants.

It is known that one way of increasing the hydrophoby of a porous material is to apply a protective coating on its surface (Japan patent application No. 62-288114, RF patent No. 2022949). It is obvious that deposition of a coating on the surface of granules (plating) should not only decrease the open porosity and, accordingly, increase the moisture resistance of granules, but should also improve the spherical shape of granules, which makes them stronger under the effect of compressive loads.

This study attempts to solve the problem of increasing the strength and hydrophoby of propants by depositing a silicate coating on their surfaces. Plating was tried on granules of size 0.63 to 0.8 mm with initial porosity about 18%. The coating deposited on the surface of granules had the form of a suspension from which highly disperse oxide powders precipitated in heat treatment.

To obtain the silicate coating, various compositions of organosilicon solutions and sodium silicate (liquid glass) were used. The coating was applied to the granules either by immersing the granules in the solution with subsequent fixation by thermal treatment, or by spray-deposition of the solution on preheated granules using an atomizer in the “pseudo-fluidized (boiling) layer” device. After the experiments the

strength of the coated granules was compared with that of initial granules.

The strength was measured in static conditions. As was earlier demonstrated [1] the simplest and most efficient way of measuring strength for glass and irregular fragments is crushing them between rigid supports. A granule is placed between two parallel planes, to one of which a certain force is applied registered by a force sensor. The value of the force that causes destruction of the granules is registered. It should be noted that the spread in values in measuring strength of granules is substantial. This is related to the specifics of the considered material: deviation of the granules from a regular geometrical shape and heterogeneity of their porous structure. Therefore, to refine the reliability of results, statistical processing of a great number of measurements is required. As a consequence of special studies on initial (uncoated) granules, it was established that 20 measurements are necessary and sufficient.

There exists a method for measuring the volume strength of granules (MR-0002–2001), in which a strictly preset number of granules of size greater than 0.63 mm is placed in a matrix of a strictly preset size. The punch experiences a load with a fixed velocity, and on reaching the required pressure, the exposure lasts 1 min. Then the load is relieved from the punch and the granules are poured on a vibrator sieve and screened for 10 min, after which the weight content of granules that have passed the sieve with a cell size of 0.63 mm is determined. The measurements are performed for several pressure levels applied to the punch.

This method has some deficiencies as well. First, it requires a great number of granules. Second, errors originate in screening and weighing. However, for a qualitative comparative study (comparison of coated and uncoated granules)

¹ Sverdlovskii Research and Development Institute of Chemical Machine-Building Joint-Stock Company, Ekaterinburg, Russia.

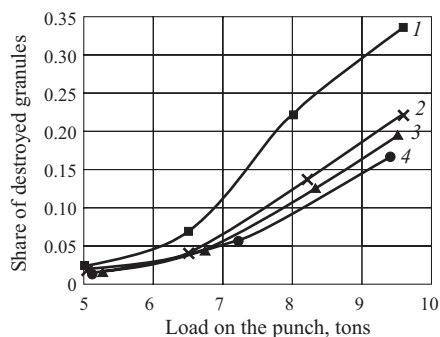


Fig. 1. Strength of granules with coatings of different thickness deposited in the pseudo-fluidized-layer machine: 1) initial granules; 2, 3, and 4) granules after 2, 4, and 6 cycles, respectively.

both strength measurement methods have yielded comparable results and were used to evaluate the degree of strengthening of granules by depositing coatings.

A microscope study of the surface of the granules indicated that in heat treatment the structure of the coating layer changes, which determines the modification of the strength of the granule. First, in heat treatment a coating based on organosilicon liquid becomes polymerized, and as the time of heat treatment increases, the coating consolidates and its adhesion increases. The strength of the granules in this case becomes higher. However, at low temperatures and with short treatment duration, the granules may even become less strong than the original granules. This is apparently related to the propping effect of liquid as it impregnates the porous material of the granule and to incomplete polymerization inside the granule under short exposure and low temperature of heat treatment. Increased treatment duration leads to condensation of the coating and increased strength of the granules.

It is established that under heat treatment shorter than 15 min, the granules become weaker. Longer heat treatment increases their strength, although there is no perceptible growth in strength of granules compared to the initial ones due to the low strength of the polymeric coating itself.

As the temperature increases, the structure of the coating starts changing, the continuity of the coating is broken, scales emerge on the surface of the granules, the coating density decreases and, accordingly, the strength of the granules does not differ much from that of uncoated granules. Increase in heat treatment duration to 30 min in this case increases the strength significantly, since the coating in time consolidates and its structure changes from a scaly to a smoother one.

Further increase in temperature (up to the silicate melting point) leads to the formation of a coating with high density and adhesion strength, which is formed from silicates resulting from decomposition of organosilicon polymers. As solutions based on organosilicon liquids have good wetting capacity, they impregnate granules, filling their pores. High-strength silicates emerge not only on the surface of the granules but also inside the pores, increasing the strength of granules and the adhesion of the coating to the surface of the granules.

With different compositions of organosilicon liquids used for preparation of solutions with an amorphous structure, one can obtain a silicate coating whose structure is represented by silicon oxide or sodium silicate. The structure of the coating depending on the heat treatment duration and the cooling rate can be either finely crystalline or amorphous. Granules with coatings obtained at a temperature of heat treatment corresponding to the melting point of silicates have a smooth, lustrous, transparent surface with an amorphous structure and are destroyed in a narrow pressure interval, which facilitates their use under industrial conditions.

It should be noted that the strength of granules in this case increases mainly due to the formation of silicates inside the pores, i.e., due to the decreased porosity of granules, which determines the narrow interval of granule destruction.

The mechanism of formation of coating from liquid glass solutions is somewhat different. Here strengthening occurs due to fusion of sodium silicate in heat treatment of the coating. In this case a coating with an amorphous structure arises with a great number of bubbles and discontinuities inside the coating. The destruction of granules with such coatings occurs mainly along the interface of the coating with the granule material due to low adhesion of the coating, which is related to the insufficient wetting capacity of liquid glass.

Figure 1 shows the volume strength of granules with coatings of different thickness obtained in the pseudo-fluidized-layer device, in which 1 cycle correlates with 1 min of operation of the atomizer. An increase in the spraying duration leads to an increased thickness of coating, which contributes to increased strength of the granules. The granules with coatings obtained in the pseudo-fluidized layer have higher strength (1.5–2 times higher under different loads) than the initial granules. However, an increase in the coating thickness requires a simultaneous increase in the duration of heat treatment for the chemical processes to be completed.

Thus, the theoretical possibility is demonstrated of increasing the strength of refractory granules by 1.5–2 times by depositing coatings based on organosilicon liquids at elevated temperatures. The increased strength is mainly achieved in the formation of coatings with the structure of fine-crystalline sodium silicate, silicon oxide, or glass; the strength of the granules increases with increasing thickness of the coatings.

Based on studies performed at the Sverdlovskii Research and Development Institute of Chemical Machine-Building JSC, a cost-effective and environmentally safe program for strengthening granules by depositing coatings in the pseudo-fluidized(boiling)-layer device has been developed. An experimental batch of granules strengthened according to the new technology was obtained in the boiling(fluidized)-layer device, and the optimum parameters were determined. The granules have increased strength, spherical shape, and hydrophobicity.

REFERENCES

1. E. D. Shchukin, A. I. Bessonov, and S. A. Paranskii, *Mechanical Testing of Catalysts and Sorbents* [in Russian], Nauka, Moscow (1971).